

Synthesis, Spectral Studies of Co (II) Complexes with Schiff base Containing N, O & S donor atoms

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Abstract:

This paper presents the formation of Schiff base by the condensation of primary amine with carbonyl compound. Schiff base complexes play a major role in stereo chemical model and coordination chemistry to their preparation accessibility diversity and structural variability¹. Co(II) complexes with chelating ligand containing N,O,S as a donor atoms have attracted special attention. The Schiff base ligand as well as cobalt2 complexes were synthesized carefully. The ligands were usually Nicotinamide Semicarbazone as well as Thiosemicarbazones³. The ligand their Co(II) Complexes were synthesized and characterized by elemental analysis, conductivity measurement, study of electronic, IR, NMR and eprSpectra. Conductivity data showed the non-electrolytic nature of ligand. Distorted Octahedral Geometry were proposed for Co(II) Complexes⁵. Their Complexes are used as model molecules for oxygen carrier crystal.

Keywords:-Schiff base, condensation, coordination, nicotinamide ,Semicarbazone, thiosemicarbazone ,nonelectolyte, octahedral.

Introduction:

Schiff base can accommodate different metal centres esp, transition metals by different coordination modes allowing successfully synthesis of Co(II) complexes with wide ranging stereo-chemistry. Schiff base derived from Semicarbazone and thiosemicarbazone and their Co(II) Complexes are of great significance for their pharmacological properties. It is documented that heterocyclic compounds play a vital role in many biological systems. Especially, N donor ligand systems, being a component of several vitamins and drugs such as nicotinamide i.e pyridine-3-carboxamide a compound of the vitamin B complex as well as a component of the coenzyme nicotinamide adenine dinucleotide (NAD). Nicotinamide is a bioligand for human health which play an important role in the metabolism of living cells and some of the Co(II) complexes are biologically active as anti-bacterial agent. Recently, nicotinamide is classified as a food additive rather than a drug. Nicotinamide also served as model compound for the conformation of polypeptides and nucleic acid.

Materials and Methods

Materials:

All of the materials were purchased from E Merck. Each of them were of analytical and R grade. The chemicals used were ethanol, nicotinamide, acetic acid, sodium acetate, Cobalt chloride ,phosphorus penta oxide, Semicarbazone, Thiosemicarbazone.

Experimental

Synthesis of ligand L1 :

About 20 mole of hot solution was mixed 0.01 mole of pyridine-3-carboxamide and then 0.01 mole of thio Semicarbazone was added in presence of 0.5 mole of acetic acid. The contents were refluxed at 70-80⁰ c for 8-10 hours on a water bath with constant stirring and cooled to get yellow precipitate. The solvent was removed and evaporated to obtained yellow solid .It was washed with ethanol and dried under vacuum over phosphorus pentoxide to get crystal.

Synthesis of ligand L2 :

About 50 ml of aqueous solution of Semicarbazone was mixed with with hydrochloride of about 0.05 mole and then added into 50 ml of ethanol solution of corresponding amide, pyridine-3-carboxamide 0.05 ml in the presence of 0,05 ml of sodium acetate. The reaction mixture was stirred vigorously for an hour .The product thus obtained was collected, washed and dried in vacuum over phosphorus pentoxide.

Synthesis of Co (II) complex:

About 0,237 gm hexahydrated Cobalt chloride or 0.29 gm of hexahydrated Cobalt nitrate was mixed with shot solution of ethanol of corresponding ligands .The mixture was refluxed for 8-10 hrs at 70-80⁰ c .The crystal thus obtained was cooled, collected, filtered washed with ethanol and dried under vacuum over phosphorus pentoxide .

Result and discussion**Physical properties:**

The analytical data of ligands and Co(II) complexes and their physical properties such colour , melting point percentage of metal, H,C ,N and molar conductance reflected the general composition of complexes, M L₂X₂ where, M is metal, L is ligand and X is Cl, NO₃ etc.

Table 1

| Complex | Colour | M.P. | Elemental analysis data pound (calculated) | | | | Molar Conductivity λ_m |
|--|-----------------|------|---|------------------|----------------|------------------|--------------------------------------|
| | | | M | C | H | N | |
| L1= C ₉ H ₉ N ₅ S | Pale Yellow | 198 | - | 42.00 (41.00) | 4.30 (4.20) | 34.9 (34.0) | - |
| L2= C ₉ H ₉ N ₅ O | Pink | 191 | - | 45.50 (45.00) | 4.90 (4.5) | 38.90 (38.00) | - |
| [Co(L1) ₂ (NO ₂) ₂] | Reddish Pink | 234 | 10.50 (10.20) | 28.60 (28.30) | 3.10 (3.00) | 28.80 (28.00) | 19 |
| [Co(L1) ₂ (Cl) ₂] | Pink | 220 | 12.06 (12.00) | 34.30 (34.00) | 3.50 (3.40) | 28.50 (28.40) | 20 |

Conductivity measurement:

The molar conductivity of Co(II) complex were found between 19-20, which indicated that the Co(II) Complexes are non electrolytes.

Electronic spectra:

The study of electronic data showed the distorted octahedral geometry of complexes.

Magnetic properties:

The magnetic properties of Co(II) complexes were observed between the range of 4.52 -5.01 BM, and corresponding 3 unpaired electrons , showed paramagnetic nature of Co(II) complexes.

Infrared spectra:

The IR bands assignment of semi carbazone and thio Semicarbazone based ligands and their Co (II) Complexes were put in the table 2 below :

Table 2

| Compound | $\nu(C = N)$ | $\nu(C = O)$ | $\nu N - H$ | $\nu(C - S)$ | $\nu M - O / M - S$ |
|--|--------------|--------------|-------------|--------------|---------------------|
| L1 | 1610 | - | 3300 | 788 | - |
| L2 | 1600 | 1650 | 3350 | - | - |
| [Co(L1) ₂ (NO ₃) ₂] | 1500 | - | 3300 | 770 | 420 |
| [Co(L1) ₂ (Cl) ₂] | 1530 | 1600 | 3100 | - | - |

The above IR data clearly indicated that the ligand act a bidentate. Chelating agent coordinating through the N of C=N group, sulphar of C=S group and O of C=O group.

epr Spectra:

The X band epr Spectra of Co(II) Complexes displayed the broad single value of g in range $g_{\pi} = 2.0001-2.0050$, $g_{\perp} = 1.9000-2.0020$ and $g_{iso} = 1.9500-2.0050$ corresponding to the tetrahedral geometry of the Complexes .

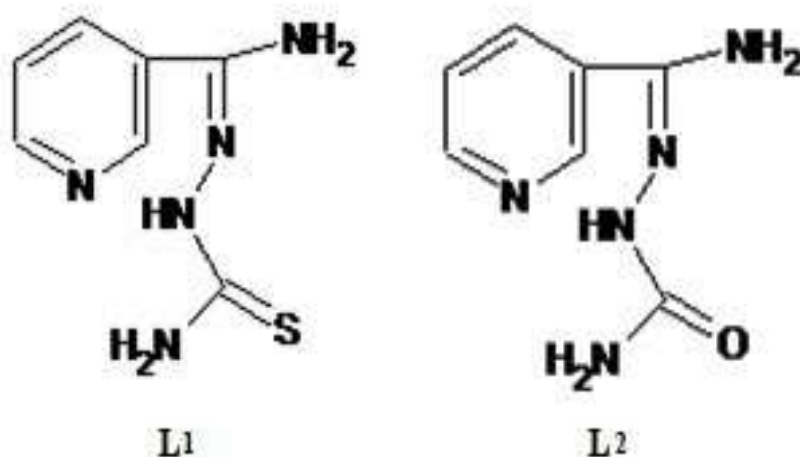
Thermal analytical data:

The total mass were observed by thermal analytical data was found as mentioned below in table 3

Table 3

| Total mass loss | Temperature |
|-----------------|------------------------|
| 85.5 % | 130-280 ⁰ C |
| 50.5 % | 288 ⁰ C |
| 14.4% | 680 ⁰ C |

Thus on the basis of spectral studies and physical measurement following structure of Co(II) complexes were suggested.



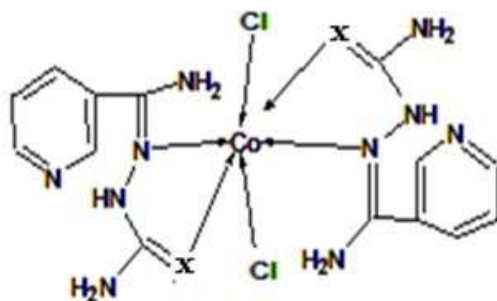


Fig. 3

Structure of $[\text{Co}(\text{L1})_2(\text{Cl})_2]$

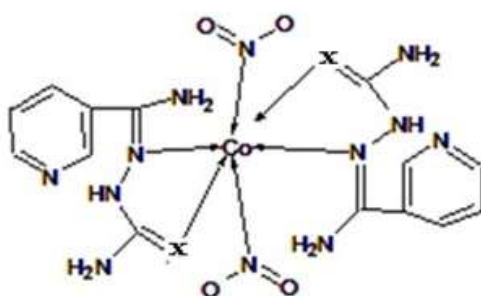


Fig. 4

Structure of $[\text{Co}(\text{L1})_2(\text{NO}_3)_2]$

Conclusion

This paper concluded that Co(II) complexes were synthesized with newly synthesized ligand. An interesting fact was their application as chelating agents. The Co(II) complexes were proposed distorted octahedral geometry on the basis of spectral studies. The ligand and complex were found to be non-electrolyte by conductivity data.

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